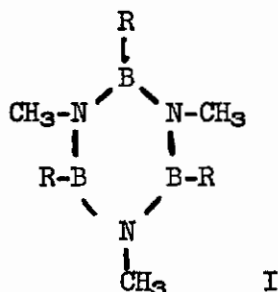# Organosilicon Derivatives of Inorganic "Benzenoid" Compounds.

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I. Introduction.

In a previous report[1] the synthesis of thermally and oxidatively stable silicon-substituted borazines (I) was reported. The present report summarizes our

$[R= (CH_3)_2R'SiCH_2-$, where $R' = CH_3$, C_2H_5, $n-C_4H_9$ and $(CH_3)_3SiO]$

further efforts in the borazine area and describes as well work devoted to the preparation of silicon-substituted phosphazenes and to the synthesis and characterization of perfluorovinyllithium. The latter reagent seemed of possible interest in connection with our studies of organofunctional borazines.

The work reported here was carried out principally by Drs. H. P. Kögler, G. Raab, W. Freyer and J. F. Helling and is being continued since September by Drs. H. Yamazaki and M. Takamizawa. The period 1 March 1959 - 30 November 1961 is covered in this summary.
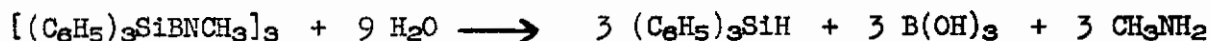
II. Discussion.
A. Preparation of Silicon-substituted Borazines.

A compound containing a B-Si linkage (I, R= $(C_6H_5)_3Si-$) was prepared by the reaction of triphenylsilyllithium in THF with B-trichloro-N-trimethylborazine[2]:

$$3(C_6H_5)_3SiLi + (ClBNCH_3)_3 \longrightarrow [(C_6H_5)_3SiBNCH_3]_3 + 3LiCl$$

This borazine, a white solid of m.p. 248-251°, was hydrolytically unstable:

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$$[(C_6H_5)_3SiBNCH_3]_3 + 9\ H_2O \longrightarrow 3\ (C_6H_5)_3SiH + 3\ B(OH)_3 + 3\ CH_3NH_2$$

Silicon-substituted borazines of higher molecule weight could be prepared by the reaction of B-chloro-B-bis(trimethylsilylmethyl)borazine with α,ω-di-Grignard reagents:

$$[R= (CH_3)_3SiCH_2-\ ;\ m.p.\ 93\text{-}94°]$$
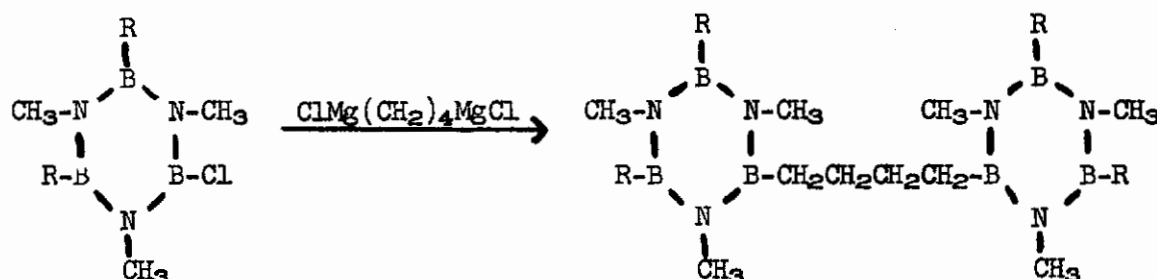
This approach to stable borazines of higher molecular weight should be applicable to other novel systems, including cross-linked polymers when B-dichloro-B-trimethyl-silylmethyl-N-trimethylborazine is used in place of the monochloro compound.
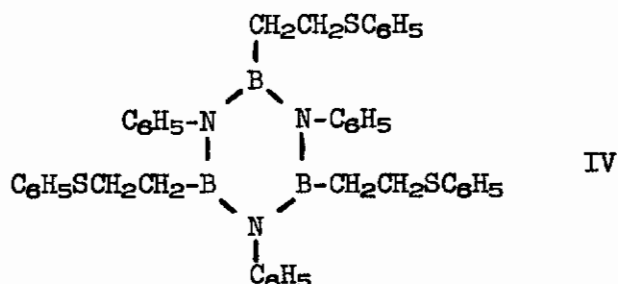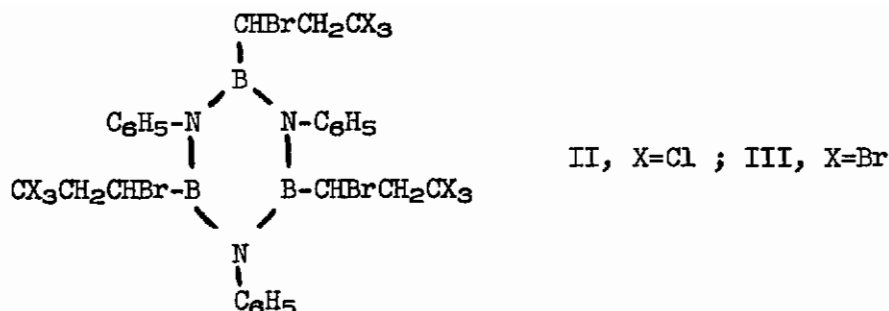
Other studies showed that facile introduction of bulky trimethylsilyl-methyl groups into borazines by the Grignard reaction is limited to those cases in which the groups on the nitrogen atom are fairly small. Thus various N-triphenyl-borazines did not react with trimethylsilylmethylmagnesium chloride or bromide, although they did react well with methylmagnesium bromide.

B. Reactions of B-Trivinyl-N-triphenylborazine.

The preparation of B-trivinyl-N-triphenylborazine has been reported and its polymerization properties have been studied.[3] We have begun an investigation of the reactions of this compound with a variety of reagents with the object of preparing a wide variety of organofunctional borazines.

It might have been expected that phenyllithium would add across the double bonds in the vinylborazine, as it does with vinylsilanes and vinylgermanes. However, this was not the case; phenyllithium appeared not only to disrupt com-pletely the borazine ring system, but also to displace the vinyl group on boron. The major boron-containing product of this reaction was triphenylborane (isolated as $(C_6H_5)_3B\cdot NH_3$).

A variety of radical reagents added to the C=C bond in B-trivinyl-N-tri-phenylborazine. These included bromotrichloromethane, carbon tetrabromide and benzenethiol, and borazines II, III and IV, respectively, were obtained. Dimethyl-phosphite and trichlorosilane reacted with the vinylborazine in the presence of peroxide initiators, but pure products have not yet been isolated. Methyldichloro-silane also added to the vinylborazine when chloroplatinic acid was used as the catalyst, but again a noncrystallizable oil resulted.

CHBrCH$_2$CX$_3$
|
B
C$_6$H$_5$-N   N-C$_6$H$_5$
| |
CX$_3$CH$_2$CHBr-B   B-CHBrCH$_2$CX$_3$
|
N
|
C$_6$H$_5$

II, X=Cl ; III, X=Br

CH$_2$CH$_2$SC$_6$H$_5$
|
B
C$_6$H$_5$-N   N-C$_6$H$_5$
| |
C$_6$H$_5$SCH$_2$CH$_2$-B   B-CH$_2$CH$_2$SC$_6$H$_5$
|
N
|
C$_6$H$_5$

IV

C. <u>Attempted Preparation of Silicon-substituted Phosphazenes.</u>

It has been reported that trimeric and tetrameric phosphonitrilic chlorides can be arylated by the Grignard and by the Friedel-Crafts procedures. However, more useful procedures for obtaining alkyl or aryl derivatives of the cyclic phosphonitrilic chlorides involve using alkyl(or aryl)**tetrachlorophos**phoranes and dialkyl(or diaryl)trichlorophoranes in place of pentachlorophosphorane in the phosphazene ring closure reaction[4]:
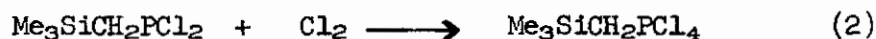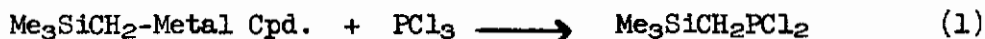
$$RPCl_4 \ + \ NH_4Cl \longrightarrow \ [NP(R)Cl]_n$$

It was decided to test this approach to organosilicon-substituted phosphazenes in this research.

The compound whose preparation was desired was:

R   Cl
\ /
P
N //   \\ N
| |
Cl   P   P   R
\   /
R N   Cl

[R= (CH$_3$)$_3$SiCH$_2$]
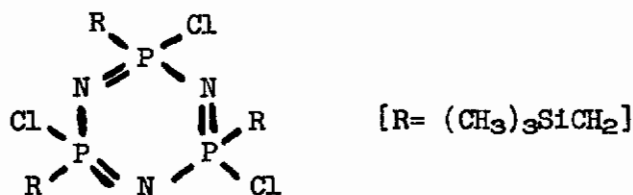
and its synthesis was attempted using the following reactions:

$$\text{Me}_3\text{SiCH}_2\text{-Metal Cpd.} + \text{PCl}_3 \longrightarrow \text{Me}_3\text{SiCH}_2\text{PCl}_2 \qquad (1)$$

$$\text{Me}_3\text{SiCH}_2\text{PCl}_2 + \text{Cl}_2 \longrightarrow \text{Me}_3\text{SiCH}_2\text{PCl}_4 \qquad (2)$$

$$\text{Me}_3\text{SiCH}_2\text{PCl}_4 + \text{NH}_4\text{Cl} \longrightarrow [\text{NP(Cl)(CH}_2\text{SiMe}_3)]_n \quad (3)$$

Conventional methods used to prepare alkyldichlorophosphines utilize the reaction of phosphorus trichloride with mild alkylating reagents such as dialkylmercury[5] or tetraalkyllead[6] compounds. Accordingly, bis-(trimethylsilylmethyl)mercury and tetrakis-(trimethylsilylmethyl)lead, both new compounds, were prepared by the usual Grignard procedure, and their action on phosphorus trichloride was investigated. The mercurial did not react with phosphorus trichloride either when a mixture of the reactants was refluxed in hexane solution, or in the absence of solvent at ca. 76°. In contrast, the lead compound was cleaved by phosphorus trichloride, giving crystalline, sublimable tris-(trimethylsilylmethyl)lead chloride and trimethylsilylmethyldichlorophosphine. However, the isolated yield of the phosphine was not very high, and a better synthesis was desired.

$$(\text{Me}_3\text{SiCH}_2)_4\text{Pb} + \text{PCl}_3 \longrightarrow (\text{Me}_3\text{SiCH}_2)_3\text{PbCl} + \text{Me}_3\text{SiCH}_2\text{PCl}_2$$
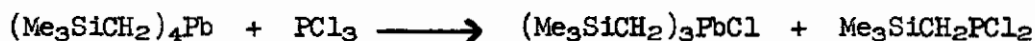
Although the Grignard procedure is not generally applicable to the preparation of pure alkyldichlorophosphines because mixtures of mono-, di- and trisubstituted products result, it seemed possible that with the relatively bulky trimethylsilylmethyl group, monosubstitution could be realized in acceptable yield. Indeed, our previous work[7] showed that complete substitution of all three chlorine atoms in phosphorus trichloride with trimethylsilylmethyl groups by the Grignard procedure requires drastic conditions. It was found in the present work that addition of one equivalent of trimethylsilylmethylmagnesium chloride to one mole of phosphorus trichloride in ether at low temperature resulted in the desired trimethylsilylmethyldichlorophosphine in ca. 40% yield. Further study of this reaction aimed at improvement of the yield was deferred until the practicality of reactions (2) and (3) could be assessed.

Attempted conversion of trimethylsilylmethyldichlorophosphine to trimethylsilylmethyltetrachlorophosphorane (reaction 2) was not successful. Even at -20° in the dark, addition of a solution of chlorine in 1,1,2,2-tetrachloroethane to trimethylsilylmethyldichlorophosphine caused cleavage of the carbon-silicon bond to form trimethylchlorosilane. This facile cleavage of the carbon-silicon bond may be due to the inductive effect of the PCl_4 group; electron withdrawal by this group would make the silicon-carbon bond more polar, hence more susceptible toward ionic fission. Investigation of the solid formed in the chlorination reaction showed it to be impure pentachlorophosphorane rather than the expected chloromethyltetrachlorophosphorane. The hydrolysis product of this solid formed a barium salt of very low carbon content, and an anilinium salt could be prepared which was shown to be $[\text{C}_6\text{H}_5\text{NH}_3][\text{H}_2\text{PO}_4]$. It is **not** known at what point fission of the phosphorus-carbon bond took place, nor is the fate of the methylene group of the trimethylsilylmethyldichlorophosphine known. It is, however, very likely that such cleavage took place after the cleavage of the silicon-carbon bond, since initial cleavage of trimethylsilylmethyldichlorophosphine at the phosphorus-carbon bond would have given chloromethyltrimethylsilane. This compound is stable to

silicon-carbon bond cleavage under these experimental conditions, although side chain chlorination does take place.
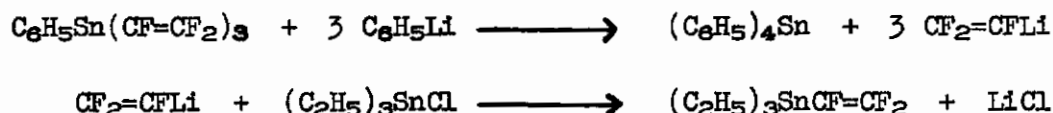
Since the proposed synthesis of silicon-substituted phosphazenes failed in the second of the three steps, this approach was abandoned.

B.   The Synthesis of Perfluorovinyllithium.

It would be most desirable to introduce unsaturated groups, such as the vinyl and the perfluorovinyl group, into borazines. Hopefully, functionality of this type would allow polymerization reactions to be carried out with the object of linking borazene rings. Also addition of various reagents to the unsaturated groups would permit the preparation of a large variety of borazines containing organofunctional alkyl groups linked to boron.

Active metal vinyl compounds - vinylmagnesium chloride and bromide, vinyl-lithium and vinylsodium - have been developed in recent years. More recently per-fluorovinylmagnesium bromide[8] was described. After our early attempts to prepare B-vinylated borazines, the synthesis of B-trivinyl-N-triphenylborazine was reported in the patent literature[3]. For this reason we initiated a study directed toward the synthesis of B-perfluorovinylborazines.

Perfluorovinylmagnesium bromide is known as a relatively unstable species that must be prepared and used in tetrahydrofuran solution[8]. It was thought that perfluorovinyllithium might be capable of existence and that this reagent might be prepared in other, lower boiling solvents, thus extending the versatility of per-fluorovinylation procedures. Our first efforts showed that perfluorovinyllithium could not be prepared by the direct reaction between metallic lithium and bromo-trifluoroethylene. Accordingly, the transmetalation procedure which had proven of exceptional utility in the synthesis of vinyllithium[9] and allyllithium[10], was applied in this case. Perfluorovinyltin compounds had been the subject of previous study in these Laboratories[11], and the action of organolithium reagents on per-fluorovinyltin compounds was examined as a possible route to perfluorovinyllithium. The reaction between triphenylperfluorovinyltin and phenyllithium, carried out in diethyl ether at room temperature, demonstrated that the exchange reaction did in-deed occur, since tetraphenyltin was isolated in nearly quantitative yield. How-ever, no evidence could be obtained for the presence of perfluorovinyllithium in the dark brown solution which was formed. Since perfluorovinyllithium did not appear to be stable under these conditions, it was felt that either lower reaction temperatures in the diethyl ether system or a change to a less polar solvent might favor the stability of the desired reagent. Subsequent experiments showed that perfluorovinyllithium could be prepared as a stable entity either in diethyl ether or in pentane at -40° to -30°. The reaction of phenyllithium with phenyltriper-fluorovinyltin (3:1 molar ratio) in ether at ca. -40° proceeded rapidly, giving a precipitate of tetraphenyltin and a brown solution of perfluorovinyllithium. Exploratory experiments showed this reagent was best characterized by its reaction with triethyltin chloride:

$$C_6H_5Sn(CF=CF_2)_3 \ + \ 3 \ C_6H_5Li \longrightarrow (C_6H_5)_4Sn \ + \ 3 \ CF_2=CFLi$$

$$CF_2=CFLi \ + \ (C_2H_5)_3SnCl \longrightarrow (C_2H_5)_3SnCF=CF_2 \ + \ LiCl$$

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The yield of triethylperfluorovinyltin obtained was ca. 40%, and this represents a minimum figure for the yield of perfluorovinyllithium in the transmetalation reaction. Perfluorovinyllithium also reacted normally with trimethylbromosilane and carbon dioxide.

A similar exchange reaction could be effected in pentane between n-butyl-lithium and n-butyltriperfluorovinyltin. However, in this solvent exchange was not complete, and it was found best to use the lithium reagent and the tin compound in 2:1 molar ratio. When the perfluorovinyllithium preparation was carried out in -30° and triethyltin chloride used to characterize the lithium reagent formed, the work-up procedure gave triethylperfluorovinyltin in 46 - 50% yield. Since the exchange was not complete under these conditions, and since in fact a deficiency of n-butyl-lithium was used, the possibility existed that triethyltin chloride could undergo direct exchange with any perfluorovinyltin compounds still present in the reaction mixture. To completely exclude this possibility the reaction mixture was shaken with aqueous-alcoholic potassium fluoride solution prior to removal of solvent and distillation of the products. This treatment removed unreacted triethyltin chloride as the insoluble fluoride. Other experiments showed that the exchange reaction between triethyltin chloride and di-n-butyldiperfluorovinyltin occurred only when this mixture was heated. Thus distillation at reduced pressure of a mixture of tri-ethyltin chloride and di-n-butyldiperfluorovinyltin produced triethylperfluorovinyl-tin in ca. 9% yield.

Perfluorovinyllithium was more stable in pentane than in ether solution. It appeared to be stable in pentane at 0°, but short refluxing of its pentane solution caused complete decomposition.

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